

(11) (A) No. 1092276

(45) ISSUED 801223

(52) CLASS 400-89
C.R. CL. 400-49

(51) INT. CL. ²C09K 3/00,
C08L 23/04,35/00, C08K 5/00

(19) (CA) **CANADIAN PATENT** (12)

(54) PROCESS FOR THE PRODUCTION OF SELF-SWELLING LEAKAGE-
PREVENTING MATERIALS

(72) Sasayama, Hiroharu,
Japan

(73) Granted to C.I. Kasei Company, Limited
Japan

4. impleg core mat

(21) APPLICATION No. 284,817

(22) FILED 770816

(30) PRIORITY DATE Japan (100388/1976) 760823

No. OF CLAIMS 7

PROCESS FOR THE PRODUCTION OF
SELF-SWELLING LEAKAGE-PREVENTING MATERIALS

Abstract of the Disclosure

A self-swelling leakage-preventing material is produced by reacting under heat a mixture of a copolymer of (a) a lower olefin, such as isobutene, with maleic anhydride, (b) a polymer emulsion having compatibility with the copolymer, such as an ethylene-vinyl acetate copolymer emulsion, and (c) a compound having at least two functional groups selected from the group consisting hydroxyl groups, amino groups and epoxy groups, such as ethylene glycol, until a cross-linked product having a swelling rate of 5-40 times is obtained. The material is useful for filling cracks, gaps, etc. in construction works, such as water distribution mains.

1092276

The present invention relates to a process for the production of a novel self-swelling leakage-preventing material capable of swelling by absorption of water and preventing leakage of water by clogging interstices.

In public works and construction works, cracks, cleavages or interstices often form in the places where mortar or concrete has been applied or wherein water-supplying pipes are jointed, and can be sources of water leakage. In the prior art, such cracks or interstices are filled with a leakage-
10 preventing filler material based on rubber, plastics and bitumen, such as rubber packing materials, rubber sealants and bitumen jointing materials. Over a long period of time, these materials tend to deteriorate so that cracks may form in the fillers themselves or gaps may occur between the fillers and the walls of the cracks being filled, again causing water leakage. A leakage-preventing material of such type as can be swollen by the leaking water and can seal interstices or pores to stop leakage of water has previously been proposed. However,
20 the prior material lacked durability because of its poor swelling rate and poor gel strength. Thus, there has not yet been found a practically advantageous leakage-preventing material for the present purpose.

Brief Summary of the Invention

In accordance with the present invention, there is provided a novel self-swelling leakage-preventing material, which is obtained by reacting under heat a mixture of (a) a copolymer of a lower olefin and maleic anhydride, (b) a polymer emulsion having compatability with the copolymer and
30 (c) a compound having at least two functional groups selected from the group consisting of hydroxy groups, amino groups and epoxy groups, until a crosslinked product having a swelling

rate of 5-40 times is obtained.

Certain preferred embodiments are illustrated by the accompanying drawings wherein:

Figs. 1 and 2 are graphs showing respectively the relation between the swelling rate and the immersion time in Example 1 and a Comparative Example.

The copolymer utilizable in the present invention as the above component (a) can be obtained by polymerizing a lower olefin such as ethylene, propylene, n-butene, isobutene, 10 1-pentene, 2-pentene or 2-hexene and maleic anhydride in a proper solvent such as dimethylformamide in the presence of a radical polymerization initiator such as a persulfate. This copolymer is advantageously converted, prior to the actual use, into a water-soluble form, for example, by neutralization with ammonia water.

The polymer emulsion utilizable as the above component (b) is a known polymer emulsion having compatibility with the component (a), for example, an ethylene-vinyl acetate copolymer emulsion or an acrylic polymer emulsion. The polymer emulsion 20 is used in an amount of 20-100 parts by weight (solid), preferably 50-60 parts by weight per 100 parts by weight of the component (a).

Illustrative of the polyhydric or polyfunctional compound as the above component (c) are, for example, ethylene glycol, propylene glycol, glycerol, glycidyl alcohol, diglycidyl ether, ethanolamine, ethylenediamine, propylenediamine, poly-ethylene glycol, trimethyloolpropane and pentaerythritol. This compound is used in an amount corresponding to 1-10 equivalent functional groups per equivalent of the carboxyl groups present 30 in the copolymer as the component (a).

In the present invention, a mixture of the above

1092276

components (a), (b) and (c) may have added thereto, if desired, a foaming agent, an antioxidant, a dye, a pigment or the like conventional additive.

A mixture prepared in this manner by mixing the individual components may have an appropriate amount of water added thereto and then be shaped into a desired form, for example, a sheet or block. Alternatively, a core material such as a nonwoven cloth, fabric, rope, knit cloth or string is impregnated with the mixture. The shaped article or the
10 impregnated core material is dried for dehydration and reacted under heat until a crosslinked product having a swelling rate of 5-40 times is obtained.

It is necessary in the present invention to continue the crosslinking reaction until the swelling rate of the resultant crosslinked product becomes 5-40 times. If the crosslinking reaction proceeds beyond the swelling rate of the above range, the resultant product will no longer function satisfactorily as a swelling leakage-preventing material. On the other hand, if the crosslinking reaction fails to proceed
20 to such stage that the product may have the above defined swelling rate, the product obtained will be poor in gel strength so that satisfactory leakage-preventing effect will not be obtained.

The reaction can conveniently be carried out for a period from 10 minutes to 8 hours at a temperature of 80-120°C, preferably 4 hours at 80°C and 1 hour at 100°C.

When the leakage-preventing material is shaped by extrusion or calendering, the content of water in the shaping composition is usually 5-40%, preferably 10-30%. When the
30 leakage-preventing material is shaped by spreading of the shaping composition or by impregnating a core material with the

1092276

shaping composition, the content of water in the shaping composition is usually 30-70%, preferably 40-60%.

Heretofore, a contradictory relation has been known between the swelling rate and the gel strength; increase of the swelling rate by absorption of water has caused reduction of the gel strength, while enhancement of the gel strength has resulted in reduction of the swelling rate. According to the present invention, however, unexpectedly remarkable advantages can be achieved in that the gel strength can
10 appreciably be enhanced without damaging the swelling rate by addition of the polymer emulsion. This is quite surprising because in the prior art, swelling by absorption of water has been considered to be harmful since the emulsion became filmy and hydrophobic after drying and the subsequent heating.

The leakage-preventing material obtained according to the present invention charged into interstices of structures has the ability to comply with any enlargement of the interstices caused by dimensional change of the structures so that the material can exhibit a stable leakage-preventing effect
20 for a long period of time. Further, the leakage-preventing material has the advantage of retaining this capability even if the material is repeatedly dried and swollen. Thus, the material is particularly suitable as a seal for filling up gaps between segments in tunnel construction, a seal for a joint portion of a flume, a seal for filling up interstices in the outer wall panels of buildings, and a wind-seal.

The present invention will now be illustrated in more detail by way of examples.

In each example, the leakage-preventing test is
30 carried out by fixing a sheet of the material between two flanges with 4 bolts at a binding pressure of 400kg/cm^2 ,

1092276

injecting water into the flanges to let the sample absorb water, increasing the clearance between the two flanges by 2mm with the aid of a spacer and injecting water under pressure.

Example 1

A non-woven polyester fabric having a basis weight of 60kg/m^2 was immersed into a liquid mixture of 100 parts by weight of isobutene-maleic anhydride copolymer (polymerization degree: 500) neutralized with ammonia water, 100 parts by
10 weight of polyethylene glycol having a molecular weight of 200, 100 parts by weight of an aqueous emulsion (50% in solid content) of ethylene-vinyl acetate copolymer and 250 parts by weight of water. The non-woven fabric was impregnated with the mixture in an amount of 600g/mm^2 and then air dried for 15 minutes at 90°C . The impregnated non-woven fabric was then heated at 80°C for 4 hours whereby a swellable leakage-preventing material (1mm in thickness) was formed.

The leakage-preventing material thus obtained was dipped for 3 hours into water kept at 20°C to permit gelation
20 and swelling of the material whereby the swelling rate was 22.0 times and the loss rate of the material from the non-woven fabric was 11.6%. As a result of a leakage-preventing test of this material, no leakage of water was observed at a water pressure of 7.5kg/cm^2 .

The relation between the immersion time (immersion days) and the swelling rate of this material is shown in Figs. 1 and 2 by a solid line.

Comparative Example

The non-woven fabric was impregnated in the same
30 manner as described in Example 1 with a liquid mixture of 100 parts by weight of the same copolymer as described in

1092276

Example 1, 100 parts by weight of the same polyethylene glycol as described in Example 1 and 300 parts by weight of water. The non-woven fabric was then treated in the same manner as described in Example 1 to prepare a swelling substance. The swelling rate of this material was 15.3 times while the loss rate of the material from the non-woven fabric was 46.3%. As a result of a leakage-preventing test of this material, leakage of water began at a water pressure of 30 kg/cm² and the water pressure was rapidly reduced.

10 The relation between the immersion time (immersion days) and the swelling rate of this material is shown in Figs. 1 and 2 by a broken line.

Example 2

To a mixture of 100 parts by weight of isobutylene-maleic anhydride copolymer (polymerization degree: 500) neutralized with ammonia water, 60 parts by weight of polyethylene glycol having a molecular weight of 200, 200 parts by weight of an aqueous emulsion (50% in solid content) of ethylene-vinyl acetate copolymer and 100 parts by weight of
20 silicon oxide powder (average particle size: 200 mesh; SiO₂ content: 97% or more) were added 5 parts by weight of water. Using 8" kneading rolls, the mixture was shaped into a sheet which was then pressed to obtain a sheet of 1mm in thickness. This article was subjected to a heat treatment conducted at 80°C for 3 hours whereby a swelling substance was prepared. As a result of a leakage-preventing test of this substance, no leakage of water was observed at a water pressure of 7.5kg/cm² as in the case of Example 1. The swelling rate of this material was 6-7 times.

30 Example 3

To a mixture of 100 parts by weight of isobutylene-maleic anhydride copolymer (polymerization degree: 500)

1092276

neutralized with ammonia water, 60 parts by weight of polyethylene glycol having a molecular weight of 200 and 200 parts by weight of an aqueous emulsion (50% in solid content) of ethylene-vinyl acetate copolymer were added 100 parts by weight of water. The mixture was shaped into a sheet according to the spreading method whereby a sheet of 1mm in thickness was obtained. The sheet was subjected to a heat treatment conducted at 80°C for 3 hours whereby a swelling substance was formed.

10 As a result of the leakage-preventing test of this substance, no leakage of water was observed as in the case of Example 1 at a water pressure of 7.5kg/cm^2 . The swelling rate of this substance was 5-6 times.

20

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A process for the production of a self-swelling leakage-preventing material, characterized by reacting under heat a mixture of (a) a copolymer of a lower olefin and maleic anhydride, (b) a polymer emulsion compatible with said copolymer, and (c) a compound having at least two functional groups selected from the group consisting of hydroxy groups, amino groups and epoxy groups, said polymer emulsion being present in an amount of 20-100 parts by weight (as solid) per 100 parts by weight of said copolymer and said compound having at least two functional groups present in an amount corresponding to 1-10 equivalent functional groups per equivalent of the carboxyl groups present in said copolymer, until, a cross-linked product having a swelling rate of 5-40 times is obtained.
2. A process according to claim 1 wherein said lower olefin is ethylene, propylene, n-butene, isobutene, 1-pentene, 2-pentene or 2-hexene.
3. A process according to claim 2 wherein said lower olefin is isobutene.
4. A process according to claim 1 wherein said polymer emulsion having compatibility with said copolymer is at least one selected from the group consisting of ethylene-vinyl acetate copolymer emulsion and a polymer emulsion of the acrylic series.
5. A process according to claim 1 wherein said compound having at least two functional groups is at least one compound selected from the group consisting of ethylene glycol, propylene glycol, glycerol, glycidyl alcohol, diglycidyl ether, ethanolamine, ethylenediamine, propylenediamine, polyethylene glycol, trimethylol-propane and pentaerythritol.

6. A process according to claim 1, 4 or 5, wherein a core material is impregnated with said mixture.

7. A self-swelling leakage-preventing material having a swelling rate of 5-40 times, said material being a cross-linked heat reaction product of (a) a copolymer of a lower olefin and maleic anhydride, (b) a polymer emulsion compatible with said copolymer and (c) a compound having at least two functional groups selected from the group consisting of hydroxy groups, amino groups and epoxy groups, said polymer emulsion being present in an amount of 20-100 parts by weight (as solid) per 100 parts by weight of said copolymer and said compound having at least two functional groups present in an amount corresponding to 1-10 equivalent functional groups per equivalent of the carboxyl groups present in said copolymer.



Fig. 1

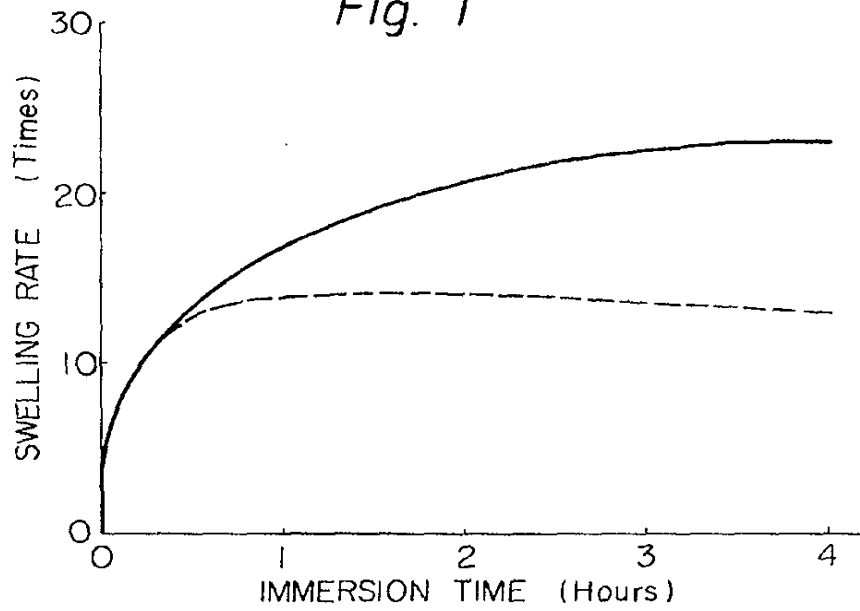
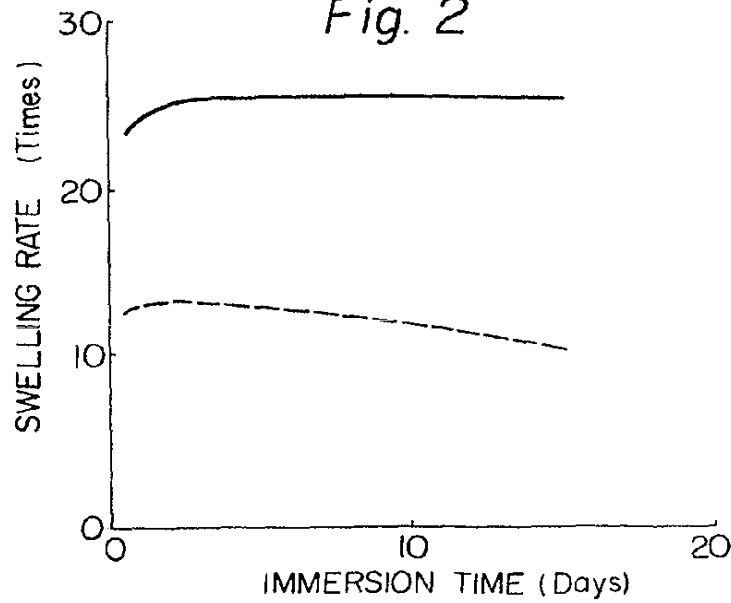


Fig. 2



Kirby Shapiro
Carphey, Eades